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Argon plasma etching of gallium nitride: spectroscopic surprises

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Abstract. It is shown that bulk reactive-ion-etched MOVPE-grown GaN can exhibit dramatically increased near-band-edge and below-band-gap emission when compared with unetched samples. A detailed spectrosopic study reveals, firstly, that donor bound excitons are the dominant species in the near-band-edge emission and, secondly, that previous models of the yellow luminescence band must be revised due to the clear linkage between the yellow emission and a little studied blue emission band. UV illumination over a period of time enhances the yellow emission by a factor of 20 at room temperature, and it is shown that this effect can be employed for optical data storage and retrieval.

Introduction

Reactive ion etching (RIE) is an important device processing technique for many semiconductors. This is especially true of Gallium Nitride (GaN), which is the material for a wide variety of opto-electronic devices in the blue-green part of the electromagnetic spectrum [1]. RIE is also a vital tool for the fabrication of GaN-based nanostructures due to its potential for precise control over etch profiles.

Despite a number of advantages over wet chemical etching methods, RIE has the potential disadvantage that it can introduce damage and/or defects, with subsequent deleterious effects on device performance. It is therefore important that RIE-induced damage in GaN is understood and controlled [2].

One of the key features of the RIE process is the interplay between chemical and physical etching mechanisms. In order to elucidate the different effects of these mechanisms we have used optical spectroscopy to examine both SF_6-etched samples (mainly chemical etching) and Ar-etched samples (physical bombardment). The SF_6-etched samples have been discussed extensively elsewhere [3]: in this paper we focus on new and surprising results from Ar-etched samples.

Experimental

Our samples are 2.5 μm thick nominally undoped GaN, grown by metal organic vapour phase epitaxy on c-plane sapphire substrates. Previous studies [3] focussed on the use of SF_6 as an etching gas with a power density of 0.45 W/cm^2, pressure 15 mtorr and flow rate 40 sccm, resulting in a DC bias of -440 V. In this work samples from two wafers were etched in an Ar-plasma (typically for 2.5 min) under conditions designed to achieve a similar DC bias (i.e. -440 V). Photoluminescence (PL) experiments were carried out on both etched and unetched samples using an argon-ion laser operating at a wavelength of 333.8 nm and a typical spot size $\sim$0.25 mm. At this wavelength, the penetration depth of the laser beam is estimated to be 100 nm [3]. Samples were mounted in a closed cycle helium cryostat and variable temperature experiments were performed in the range 24 K to 300 K.

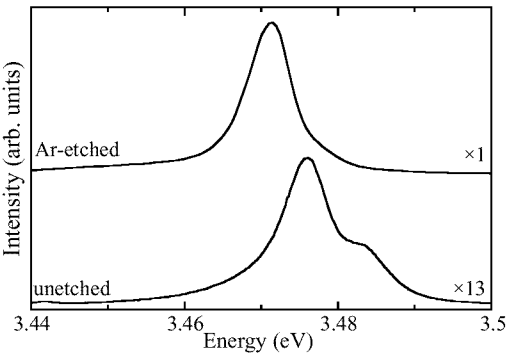

Fig. 1. Comparison of band edge PL spectra at 24 K. Note the multiplier on the right hand side.

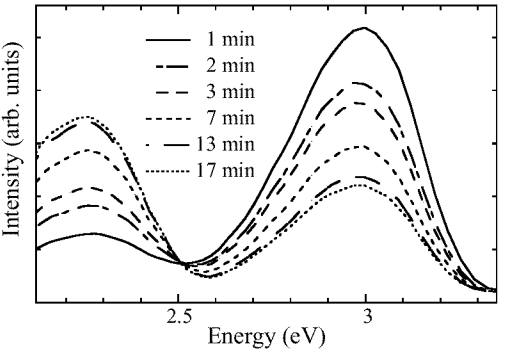

Fig. 2. Evolution with time from blue (~3.0 eV) to yellow luminescence (~2.2 eV) from Ar-etched GaN at 24 K.

Results

Figure 1 shows the band edge PL at 24 K in detail. The unetched sample shows the A_1 exciton at 3.477 eV, B_1 exciton at 3.483 eV, and negligible luminescence from bound excitons [3]. The temperature dependence of the spectra from the etched samples [3] allows us to identify the peak at 3.471 eV with the donor bound exciton (D^0X). Spectra from these Ar-etched samples are more than an order of magnitude more intense than from unetched samples and spectra are dominated by the D^0X peak, indicating an enormous increase in the number of donors in these samples. The free excitons A_1 and B_1 have not been eliminated: they are masked by the D^0X peak at low temperatures and are revealed again at elevated temperatures [4].

The increase in near-band-edge emission in the Ar-etched sample is accompanied by a dramatic increase in the strength of the defect-related yellow emission (compared to the unetched sample) [4]. However, even this effect is dominated by a dramatic time dependence of the below band gap emission that is clearly visible to the naked eye: the illuminated spot is initially bright blue and becomes bright yellow after a few minutes. Figure 2 shows a very clear transfer of intensity from blue luminesence (BL) at ~3.0 eV to yellow luminescence (YL) at ~2.2 eV as a function of time. Similar time-dependent behaviour is observed in other samples etched with an Ar-plasma using different DC biases.

In the remainder of this paper we focus on results from a single sample with dimensions ~6×~6 mm [5]. One half was reactive-ion-etched with an argon plasma (as described

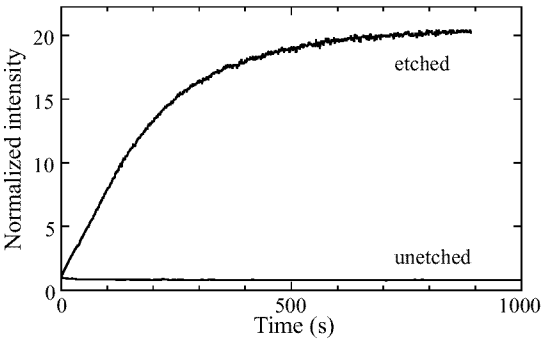

Fig. 3. Normalised YL at room temperature as a function of time while exposing etched and unetched parts of the sample to the 50 mW UV write beam.

above) for 2.5 minutes while the other half of the sample was masked and thus remained unetched. The sample was mounted on a motorised stage so that it could be moved horizontally through the illuminating laser beam while simultaneously measuring the BL or YL (c.f. Ref [6]).

By illuminating various parts of the sample, the transfer of intensity from the BL to the YL has been used to record 'data'. Data writing was achieved with high-intensity (usually 8 mW) 333.8 nm UV light while a low-intensity spot (100 μW, same diameter) was used to read the data. At low temperature, the written data were visible to the naked eye (yellow emission from previously exposed regions of the sample, blue emission elsewhere) or by setting the spectrometer to record either the BL or YL as a function of position on the sample [5]. We focus here on the results at room temperature (where no BL is observed).

Figure 3 shows that the YL from the etched sample can increase by more than a factor of 20 over 1000 seconds, but that there is very little change in the YL from the unetched sample. Figure 4 shows the YL recorded during spatial scans across the etched part of the sample before (top) and immediately after (second trace) writing at various points. Enormous peaks in YL are clearly visible from the exposed parts of the sample. At room temperature the enhanced YL from the exposed parts of the sample decays more quickly than at low temperature [5] but the features are still clearly observable more than 16 hours after writing (Fig. 4 bottom).

Discussion and conclusions

The results clearly show that reactive ion etching with an Ar-plasma can actually increase the near-band-edge emission from GaN, in contrast with the expectation that etch-induced-damage will decrease the band edge PL. It is possible that Ar-plasma etching, or post-fabrication exposure of devices to an Ar-plasma, could be used to increase band edge emission.

The transition from the BL to YL is clearly due to the introduction of metastable defects during the etching process. In fact, a BL band has commonly been observed in unetched GaN [7] in conjunction with the YL but its possible importance seems not to have been widely recognised. Any model of the YL must also be able to account for the existence of the BL and allow for the possibility of a transfer of intensity from the BL to YL. This is an important result because, despite intensive investigation over the past 30 years, no existing model of the YL [8] appears capable of explaining the key features of the data reported here.

Finally, we have demonstrated that the metastable defects created in Ar-etched samples

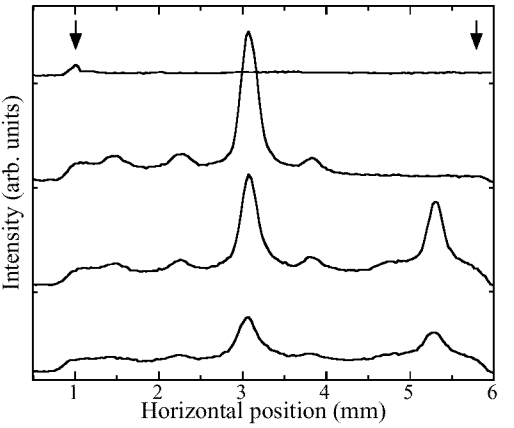

Fig. 4. YL at room temperature read with $P = 100$ μW, as a function of horizontal position across the etched half of the sample. Top: before writing; second trace: immediately after writing with $P = 5$ mW for 15 min at positions 1.0, 1.5 and 2.3 mm, with $P = 50$ mW for 15 minutes at 3.1 mm, and $P = 100$ μW for 2 min at 3.8 mm; third trace: after about 2 hours and additional writing with $P = 100$ μW for 10 min at 4.7 mm and $P = 15$ mW for 37 min at 5.3 mm; bottom: after 16 hours it is still possible to read the data. Arrows indicate the edges of the sample.

can be employed in an all-optical data storage and retrieval scheme, even at room temperature. Some alternative schemes have been reported elsewhere, but in those cases the optical memory effect relies on either InGaN heterostructures [9] or near-band-edge emission [6]. The crucial feature of the present data is the dramatic sensitisation of the material to UV exposure after etching.

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